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Background Levels of Heavy Metals in Ohio Farm Soils

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INTRODUCTION

Application to cropland is rapidly becoming the major method of sewage sludge disposal in the United States. This is especially true in Ohio. Sewage sludges are good sources of nitrogen, phosphorus and, to a lesser extent, potassium and trace nutrients, and can be significant sources of nutrients to farms in the vicinity of the sewage treatment plants producing the sludge. Land application costs are generally borne by the producer, and sludge is usually provided free of charge to the farmer. In most cases, the sewage treatment authority (*e.g.,* the municipality) also has the responsibility for spreading the sludge.

In addition to valuable nutrients and organic matter, sludges contain variable quantities of trace elements, including the so-called "heavy" metals. Most elements can be found in sludge, but the ones which have received the most attention are: cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), and lead (Pb). Of these, copper, nickel, and zinc are phytotoxic at high concentrations, *i.e.,* they reduce the growth of plants, while cadmium and lead are food-chain contaminants. Copper is also toxic to certain livestock. Of the food-chain contaminants cadmium and lead, only cadmium can readily enter the food-chain via plant uptake. It is more plant-available in soils than most metals and uptake is not restricted by plant phytotoxicity. Lead, on the other hand, is very insoluble in soil and is not readily taken up by plants. The major pathway by which lead enters the human food-chain is by direct ingestion of lead-contaminated soil or lead-containing materials. Lead poisonings of children in urban areas from ingestion of contaminated soil or lead-based paints have been reported. Soil contamination has been attributed to accumulation from paint debris in urban renewal areas and atmospheric deposition of lead from automobile emissions in high intensity transportation areas.

As metal additions to soils increase with planned or unknown applications of wastes containing metals, the testing of soils for metal concentrations will increase. Analyses may include total metals or some mea-

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sure of plant-available metals. In order to interpret the results of soil tests in terms of previous metal contamination, the natural metal levels in the soil (background concentrations) must be known. While published data for other regions may be helpful in establishing background metal levels, it is important to have information that is specific for Ohio.

Background (uncontaminated) levels of heavy metals in soils are low (in the $\mu g/g$ range or less) and are related to the geochemistry of the parent materials. Worldwide values have been published, and are given later in this paper for comparison with Ohio data. Major sources of localized heavy metal contamination of soils include:

1. Previous use of metal-containing pesticides such as copper sulfate or lead arsenate.
2. Atmospheric deposition downwind from metal smelters. Concentrations can be very high, but follow a predictable pattern in relation to the smelter.
3. Atmospheric deposition from automobile exhausts (Pb) in the vicinity of major highways.
4. Accumulation of Pb from lead-based paint in soils of urban renewal areas. The paint accumulates as debris when older buildings are demolished.
5. Trace amounts of metals (including Cd) are natural constituents of the phosphate rocks from which commercial phosphate fertilizers are made.
6. Land application of industrial and municipal wastes, primarily municipal sewage sludges.

As part of a 5-year project on land application of sewage sludges sponsored by the Ohio Farm Bureau Federation and the U. S. Environmental Protection Agency, a number of farms in several regions of the state were studied. These farms were selected only on the basis of the participants' willingness to cooperate in the study and only farms that had never previously received sludge were included. A total of 239 fields were sampled in seven counties (Figure 1), with the largest number (96) in Pickaway County. These counties are located in most of the major parent material regions of the state: Defiance in the Lake Plain; Clark, Madison, and Pickaway in the High Lime Glacial Till; Medina in the Low Lime Glacial Till; Muskingum in the Sandstone and Shale Unglaciated Region; and Franklin in both the High and Low Glacial Till Regions. Since these sites were selected at random with respect to those factors which might affect heavy metal levels (prior use of phosphate fertilizers, proximity to transportation corridors or industrial atmospheric sources, etc.), heavy metal levels for these 239 soil

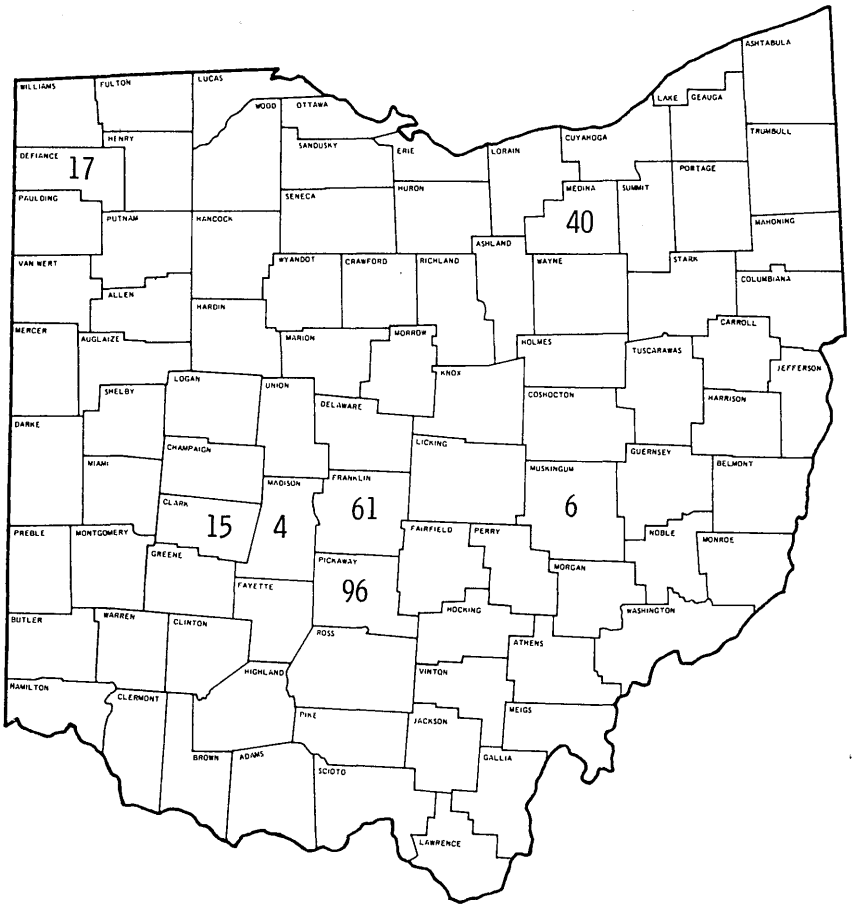

FIG. 1.—Number of farms sampled by county.

samples should provide a reasonable estimate of background metal levels for Ohio soils.

METHODS

The soil samples were taken from designated fields in the period 1977-1982. A single composite surface (0-15 cm) sample was taken from each field. The composite consisted of 30-50 cores (depending on the size of the field) which were hand mixed in a bucket. A 1,000 gram sample of the mix was then placed in a polyethylene bag and taken to the laboratory. The sample was air-dried, ground with a wooden roller, and screened to pass a 2-mm sieve. The screened soil

was stored in sealed cardboard containers until analyzed. The 239 samples were analyzed for the following:

Analysis	Number of Samples
Total Cd, Cu, Ni, Pb, Zn	239
Total Cr	186
DTPA Cd, Cu, Ni, Pb, Zn	59
Total K	53
Total P	26
Total Kjeldahl Nitrogen	25
Bray Pl Available Phosphorus	23
pH	23

pH: 1:1 in water

Bray Pl Available P: Knudsen (4). Absorbance measured at 730 nm instead of 660 nm. Detection limit 1.0 μg P/g soil.

Total Kjeldahl Nitrogen: Bremner (3). Digestion with concentrated H_2SO_4 and catalyst ($K_2SO_4/CuSO_4/Se$) on Labconco microkjeldahl digestion apparatus. Neutralize with 10*N* NaOH and steam-distill into boric acid. Titrate with 0.01*N* HCl. Detection limit 100 μg N/g soil.

Total Metals: A 2-g sample of soil is placed in a 100 ml pyrex glass tube in a machined aluminum block on a hot plate in a perchloric acid hood. Five ml of concentrated perchloric acid are added, the tube covered with a small glass funnel for refluxing, and the sample digested for 75 minutes at 200° C. After cooling, the sample is filtered with No. 1 filter paper, brought to 50 ml in a precalibrated test tube, mixed, and metals analyzed by atomic absorption spectroscopy. The six metals (Cd, Cu, Cr, Ni, Pb, Zn) were all analyzed on a Varian Model 375 spectrophotometer with an air-acetylene flame and background correction. Detection limits for the metals were: Cd—0.25; Ni—1.25; Pb—4.0; Cu—2.0; Cr—2.0; Zn—3.0 μg/g soil.

Total Phosphorus: An aliquot of the filtered perchloric acid digest for total metals which was diluted to 50 ml is further diulted 50-100 fold as needed and P is analyzed as ascorbic acid reduced phosphomolybdate at 730 nm. Detection limit 25 μg P/g soil.

Total Potassium: An aliquot of the filtered perchloric acid digest for total metals which was diluted to 50 ml is further diluted 25 fold and K is determined by flame emission on the Varian Model 375 spectrophotometer. Detection limit 200 μg K/g soil.

DTPA Extractable Metals: Soils were extracted with 0.005*M* DTPA (diethylene triaminepentaacetic acid), 0.1*M* triethanolamine and

0.01*M* $CaCl_2$ at pH 7.3 according to Lindsay and Norvell (5). The extracted metals were analyzed as for total metals. Detection limits were: Cd—0.02; Ni—0.10; Pb—0.32; Cu—0.16; Cr—0.16; Zn—0.24 $\mu g/g$ soil.

The data were analyzed statistically with Statistical Analysis System (SAS) computer programs at The Ohio State University Computer Center.

RESULTS

The range, mean, and standard deviations of the analytical parameters are given by county in Table 1 and the overall values are given in Table 2. A statistical analysis of the data showed that there were significant differences between counties for some parameters, and these are shown in Table 3. There were no consistent trends toward higher metals in one county vs. another. Some metals were significantly higher in one or more counties while other metals were highest in other counties. While there were significant differences in metal levels between the counties studied, these differences are small compared to the amounts of heavy metals that are commonly added to the soil in sewage sludges. The overall means in Table 2 are probably adequate as estimates of background heavy metal levels for the state.

Partial correlations between the analytical parameters are presented in Table 4. Only those correlations that were significant at the 0.01 level are included. DTPA extractable Cd, Cu, and Zn were correlated with the total amounts of those metals, but similar correlations for Pb and Ni were not significant. An examination of the data in Table 2 shows that all of the cadmium was DTPA extractable while 11.6, 13.7, 5.0, and 2.4% of the total Cu, Pb, Ni, and Zn, respectively, were extracted by DTPA. Soil pH was negatively correlated with DTPA Ni and Zn, and total P was positively correlated with lead.

Table 5 compares the total metal levels found for Ohio soils with other literature values. The values are quite consistent except those for chromium which were much lower in the Ohio and Minnesota studies than those reported by Allaway (1) or Baker and Chesnin (2).

Background heavy metal concentrations can be useful in determining if a soil has been contaminated by metals. Values greater than two or three times the mean background levels should be indicative of metal contamination. This study did not identify any major regional differences in soil heavy metal concentrations which would indicate areas where metal levels were naturally higher than others; however, the present study did not attempt to cover all soil parent material regions in the state.

TABLE 1.—Background Analyses by County of pH, Nutrients (μg/g), and Heavy Metals (μg/g).

	Number of Samples	Mean	Standard Deviation	Minimum	Maximum
			CLARK		
pH	0				
Bray Pl	0				
Total P	0				
TKN*	0				
Total K	0				
DTPA Cu	0				
Cd	0				
Pb	0				
Ni	0				
Zn	0				
Total Cu	15	14	2	11	19
Cd	15	<0.1	0.1	BDL†	0.1
Pb	15	14	1	11	16
Ni	15	15	2	11	18
Zn	15	61	9	47	87
Cr	15	12	6	6	23
			DEFIANCE		
pH	0				
Bray Pl	0				
Total P	0				
TKN	0				
Total K	1	10500		10500	10500
DTPA Cu	8	3.2	1.2	1.9	4.9
Cd	8	0.88	1.22	0.14	3.61
Pb	8	2.5	0.7	1.9	4.2
Ni	8	1.5	0.6	0.7	2.6
Zn	8	2.3	1.4	0.7	4.8
Total Cu	17	23	5	14	30
Cd	15	0.4	0.7	BDL	2.9
Pb	17	15	3	9	21
Ni	17	22	5	10	32
Zn	17	79	17	47	103
Cr	15	18	4	11	23

*Total Kjeldahl nitrogen.
†Below detection limit.

TABLE 1 (Continued).—Background Analyses by County of pH, Nutrients (μg/g), and Heavy Metals (μg/g).

	Number of Samples	Mean	Standard Deviation	Minimum	Maximum
		FRANKLIN			
pH	0				
Bray Pl	0				
Total P	0				
TKN	0				
Total K	2	7000	54	7000	7000
DTPA Cu	2	2.8	0.8	2.3	3.4
Cd	2	0.10	0.01	0.09	0.11
Pb	2	2.0	0.2	1.9	2.1
Ni	2	1.3	0.5	0.9	1.7
Zn	2	1.5	0.3	1.3	1.7
Total Cu	61	19	0.3	13	30
Cd	61	0.1	0.1	BDL	0.8
Pb	61	17	3	10	26
Ni	61	18	4	12	29
Zn	61	77	16	48	138
Cr	59	12	3	5	22
		MADISON			
pH	0				
Bray Pl	0				
Total P	0				
TKN	0				
Total K	0				
DTPA Cu	0				
Cd	0				
Pb	0				
Ni	0				
Zn	0				
Total Cu	4	19	2	17	21
Cd	4	0.1	0.1	BDL	0.3
Pb	4	17	1	15	18
Ni	4	20	4	14	23
Zn	4	73	5	67	79
Cr	4	12	2	10	15

TABLE 1 (Continued).—Background Analyses by County of pH, Nutrients (μg/g), and Heavy Metals (μg/g).

	Number of Samples	Mean	Standard Deviation	Minimum	Maximum
			MEDINA		
pH	17	6	0	5	7
Bray Pl	17	22	13	8	54
Total P	20	590	120	400	1010
TKN	19	2200	2100	1100	7900
Total K	25	6300	1300	4200	8700
DTPA Cu	25	1.9	1.4	0.9	7.7
Cd	25	0.10	0.04	0.03	0.20
Pb	25	2.7	0.3	1.9	3.2
Ni	25	0.6	0.3	0.3	1.7
Zn	25	1.2	0.3	0.7	2.0
Total Cu	40	17	5	11	37
Cd	40	0.2	0.2	BDL	0.6
Pb	40	23	8	11	39
Ni	40	20	4	13	29
Zn	40	75	10	54	95
Cr	15	7	1	4	9
			MUSKINGUM		
pH	6	6	1	5	7
Bray Pl	6	26	13	9	39
Total P	6	560	110	390	710
TKN	6	1500	400	1100	2100
Total K	6	4900	500	4200	5400
DTPA Cu	6	1.3	0.6	0.7	2.5
Cd	6	0.09	0.05	0.06	0.19
Pb	6	3.3	2.4	1.7	7.9
Ni	6	0.6	0.5	0.2	1.5
Zn	6	2.1	2.3	0.5	6.6
Total Cu	6	16	2	13	19
Cd	6	0.3	<0.1	0.2	0.4
Pb	6	33	3	28	36
Ni	6	25	4	20	29
Zn	6	74	10	65	92
Cr	0				

TABLE 1 (Continued).—Background Analyses by County of pH, Nutrients (μg/g), and Heavy Metals (μg/g).

	Number of Samples	Mean	Standard Deviation	Minimum	Maximum
		PICKAWAY			
pH	0				
Bray Pl	0				
Total P	0				
TKN	0				
Total K	18	6300	1300	3900	9800
DTPA Cu	18	2.3	0.6	1.3	3.7
Cd	18	0.12	0.03	0.09	0.20
Pb	18	2.5	0.7	1.5	3.9
Ni	18	1.1	0.4	0.6	2.4
Zn	18	2.3	2.4	1.0	11.2
Total Cu	96	20	5	12	36
Cd	96	0.2	0.2	BDL	1.0
Pb	96	17	3	11	27
Ni	96	17	5	9	38
Zn	96	74	14	47	130
Cr	78	11	3	5	20

TABLE 2.—Background Analyses for All Farms for pH, Nutrients (μg/g), and Heavy Metals (μg/g).

	Number of Samples	Mean	Standard Deviation	Minimum	Maximum
pH	23	6.4	0.48	4.7	7
Bray Pl	23	23	13	8	54
Total P	26	580	120	390	1010
TKN	25	2100	1800	1100	7900
Total K	52	6300	1400	3900	10500
DTPA Cu	59	2.2	1.2	0.7	7.7
Cd	59	0.21	0.50	0.03	3.61
Pb	59	2.6	0.9	1.5	7.9
Ni	59	0.9	0.5	0.2	2.6
Zn	59	1.8	1.6	0.5	11.2
Total Cu	239	19	5	11	37
Cd	237	0.2	0.3	BDL	2.9
Pb	239	19	5	9	39
Ni	239	18	5	9	38
Zn	239	75	15	47	138
Cr	186	12	4	4	23

TABLE 3.—Differences in the Total and DTPA Extractable Heavy Metal Contents of Farm Soils by County.

	Total					DTPA				
	Cu	Cd	Pb	Ni	Zn	Cu	Cd	Pb‡	Ni	Zn‡
	μg/g									
Clark	14c*	<0.1c	14d	15b	79a	†				
Defiance	23a	0.4a	15dc	22a	61b	3.2a	0.88a		1.5a	
Franklin	19b	0.1bc	17c	18b	77a	2.8ab	0.10b		1.3a	
Madison	19bc	0.1bc	17dc	20ab	73ab	†				
Medina	17c	0.2b	23b	20ab	75a	1.9b	0.10b		0.6b	
Muskingum	16c	0.3ab	33a	25ab	74ab	1.3b	0.09b		0.6b	
Pickaway	20b	0.2b	18c	17b	74a	2.3ab	0.12b		1.1a	

*Means in each vertical column with the same letter are not significantly different at the 0.05 level.
†DTPA extractable heavy metals were not measured in Clark and Madison counties.
‡There were no significant differences between counties for DTPA Pb and Zn.

TABLE 4.—Partial Correlation Coefficients for All Parameters at the 0.01 Level of Significance.

				Total						DTPA				
		pH	Total P	Cu	Cd	Pb	Ni	Zn	Cr	Cu	Cd	Pb	Ni	Zn
pH													—0.57	—0.77
Total	P					0.69								
Total	Cu				0.29		0.66	0.67	0.57	0.83			0.65	
	Cd			0.29		0.30	0.32	0.31	0.19		0.94			
	Pb		0.69		0.30		0.40	0.28	0.29				—0.35	
	Ni			0.66	0.32	0.40		0.69	0.52					
	Zn			0.69	0.31	0.28	0.69		0.37	0.51			0.52	0.56
	Cr			0.57	0.19	0.29	0.52	0.37						
DTPA	Cu			0.83	0.94			0.51					0.73	0.40
	Cd				0.94									
	Pb													
	Ni	—0.57		0.65		—0.35		0.52		0.73				0.53
	Zn	—0.77						0.56		0.40			0.53	

TABLE 5.—Comparison of Ohio Background Heavy Metal Soil Concentrations with Published Values from Other Areas.

	Ohio		Allaway (1)*		Baker and Chesnin (2)*		Dowdy et al. (4)†	
	Mean	Range	Mean	Range	Mean	Range	Mean	Standard Deviation
	Total Metal Concentration (μg/g)							
Cd	0.2	0-2.9	0.06	0.01-7	0.5	0.01-0.70	0.39	0.17
Cu	19	11-37	20	2-100	20	2-100	23	4
Cr	12	4-23	100	5-3000	200	5-1000	39	29
Ni	18	9-38	40	10-1000	40	5-500	18	10
Pb	19	9-39	10	2-200	10	2-200		
Zn	75	47-138	50	10-300	50	10-300	60	14

*Numerous sources worldwide.
†Background levels from uncontaminated soils in Minnesota. Ranges were not given.

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